Rh-catalyzed P–P bond activation[†]

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A Rh-catalyst derived from $(NacNac)Rh(COE)(N_2)$ effects the hydrogenation and silvlation of P–P bonds to give secondary phosphines and silvlphosphines, (Ph_2PH) and $(Ph_2PSiRR'_2)$ respectively; the latter process is shown to also involve the silvlation of secondary phosphines.

The impact of organometallic chemistry and catalysis on organic chemistry has been dramatic, as is evidenced by the awarding of Nobel Prizes in 2001 and 2005. A related area, ripe for impact, involves the application of the concepts of organometallic chemistry to main group synthesis and materials chemistry. Such "inorganometallics" has drawn some recent attention.¹ While much of the work to date has involved stoichiometric transformations, some catalytic processes are emerging.²⁻⁵ For example, we previously reported the use of $[Cp*_2ZrH_3]^{-6-8}$ and CpTi(NPt-Bu₃)(C₂H₄)₂ as precatalysts for the dehydrocoupling of primary and secondary phosphines, affording a variety of P-P bonded oligomers.9 In a similar fashion, Harrod and co-workers showed that titanocene derivatives can act as catalysts for the heterocoupling of silanes and phosphines.^{10,11} A recent report by Waterman and co-workers highlights the catalytic heterocoupling of primary phosphines and silanes by a Zr(IV) triamidoamine complex.¹⁵ Waterman and Tilley have also reported similar use of zirconocene and hafnocene complexes to effect catalytic dehydrocoupling of stibines, affording oligostibines.¹² Brookhart and Bohm have also probed similar dehydrocoupling of secondary phosphines using the Rh precatalyst Cp*Rh(CH₂=CHSiMe₃)₂,¹³ although this system gave only high yields for select phosphines under harsh conditions. Most recently, Han and Tilley have reported dehydrocoupling of phosphines using a catalyst based on the Rh(iPr2PCH2CH2PiPr2) fragment.14 In related chemistry, stoichiometric functionalizations of P-P bonds have been investigated to some extent;16 metal-mediated reactions involving the activation of P-P bonds has drawn less attention. We have recently examined the stoichiometric reactivity of Ni and Fe β-diketiminates with P-H and P-P bonds.¹⁷ In this paper, we report the discovery of a catalyst for the activation of P–P bonds derived from the β-diketiminate-complex Rh(NacNac)(C₈H₁₄)N₂ 1.¹⁸

In initial trials, we attempted to probe the utility of 1 in the dehydrocoupling of Ph_2PH . Over a 12 h period at 70 °C compound 1 proved to be a poor catalyst for such dehydrocoupling, giving P_2Ph_4 in only 30% yield. We hypothesized that the steric demands of the NacNac ancillary ligand

 $(NacNac = HC(CMeN(iPr_2C_6H_2))_2)$ favor non-productive P-H elimination over dehydrocoupling to give P-P bond formation. This supposition prompted us to probe the catalytic activity of 1 in reactions with diphosphine substrates. Treatment of P₂Ph₄ under 4 atm of H₂ with 10 mol% of 1 at 50 °C resulted in the hydrogenation of the P-P bond to give Ph₂PH in 95% yield in 12 h (Scheme 1). In a similar fashion, the product Ph₂P(SiPh₂H) was also prepared in 98% yield using 10 mol% 1 to catalyze the activation of P₂Ph₄ in the presence of 5 equivalents of Ph₂SiH₂ at 100 °C for 48 h (Scheme 1). Analogous use of PhMe₂SiH gave the phosphine Ph2P(SiPhMe2) in 95% yield with 5% of the by-product Ph₂PH, while bulkier silanes resulted in lower yields of the silvlphosphine. For instance, use of Ph2MeSiH or Ph3SiH gave 76% and 74% of the P-Si coupled products Ph₂P(SiPh₂Me) and Ph₂P(SiPh₃) together with 17% and 25% yield of Ph₂PH, respectively. Alkylsilanes proved to be less reactive. Et₃SiH resulted in conversion of P₂Ph₄ to 16% of Ph₂PSiEt₃ with 44% Ph₂PH, while *i*Pr₃SiH afforded no P-Si coupling product and only 29% Ph₂PH.

To garner further information regarding these P-P bond activations, the catalyst precursor 1 was reacted stoichiometrically with P₂Ph₄ in toluene and allowed to stir overnight at 25 °C. Subsequent work-up gave a dark-red residue which was recrystallized from pentane to give dark-red crystals of 2 in 50% vield. 1 It should be noted that this diminished yield is due to loss during crystallization as NMR data for reaction mixtures show near quantitative formation of **2**. This product exhibits a single ${}^{31}P{}^{1}H$ resonance at -51.4 ppm with a Rh–P coupling of 140 Hz. The ¹H NMR data for 2 was consistent with the presence of a 1 : 1 ratio of NacNac and P₂Ph₄. An X-ray diffraction study confirmed the formulation of 2 as Rh(NacNac)(P₂Ph₄) (Scheme 2, Fig. 1). The N₂P₂ coordination sphere about Rh is a distorted square-plane. The Rh-N distances of 2.054(3) Å and 2.065(3) Å are slightly shorter than those seen in the precursor 1 (2.076(3) Å and 2.074(3) Å) suggesting that the (P_2Ph_4) fragment has weaker trans



Scheme 1 Hydrogenation and silylation of P₂Ph₄ catalyzed by 1.

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Scheme 2 Synthesis of 2, 3 and 4.



Fig. 1 ORTEP depictions of (a) 2, and (b) 3.

influence than cis-cyclooctene and N2. The NacNac ligand bite angle in 2 is 90.53(11)°, while Rh–P distances are 2.2301(10) Å and 2.2423(10) Å. The P-P bond in 2 is 2.1389(14) Å and is comparable to the P-P bond in [Ni(NacNac)₂(P₂Ph₂)] (2.125(3) Å).¹⁷ The RhP₂ ring gives rise to a P-Rh-P angle of 57.14(4)° and thus the squareplanar geometry about Rh is distorted with pseudo-trans N-Rh-P angles of 160.02(8)° and 162.37(9)° and pseudo-cis N-Rh-P angles of 107.38(9)° and 106.23(8)°. The steric crowding of the Rh coordination sphere is further evidenced from the twisting of the RhP₂ plane with respect to the RhN₂ plane by 14.8°. The presence of the η^2 -P₂Ph₄ to a single metal center in **2** appears to be unique in that literature precedent demonstrates the propensity of P_2Ph_4 to bind in a monodentate fashion, or to bridge two metal centers.¹⁹⁻²⁹ In addition, the related complex Ni(NacNac)(Ph₂PH)¹⁷ binds only one phosphine ligand yielding the three coordinate species, presumably a result of the slightly larger atomic radius of Rh as well as the aforementioned geometry distortions which accommodate the η^2 -P₂Ph₄.

Reactions with P_2Et_4 seem to support partial dissociation of the P_2 fragment as a key step in the reaction. While attempts to carry out catalytic P–P activation reactions with P_2Et_4 proved unsuccessful, the species Rh(NacNac)(P₂Et₄) **3**, the analog of **2**, was readily formed in a stoichiometric reaction of P_2Et_4 with **1**

(Scheme 2). The metric parameters in **3** were found to be similar to those in **2**, with Rh–N distances of 2.064(2) Å and 2.067(2) Å and Rh–P bond lengths of 2.2229(11) Å and 2.2466(10) Å, while the P–P distance was determined to be 2.1254(14) Å. These latter observations suggest that the smaller, more basic diphosphine binds to Rh more strongly, precluding the partial dissociation that initiates subsequent P–P cleavage reactions.

Addition of H₂ to solutions of **2** resulted in no observable reactions at ambient temperatures, further suggesting that reaction of P₂Ph₄ requires thermal dissociation of the η^2 -P₂Ph₄ to at least an η^1 -P₂Ph₄ to permit oxidative addition at Rh.

In the case of H₂ reactions, the transient Rh(NacNac)(η^{1} -P₂Ph₄) has a vacant coordination site permitting oxidative addition of H₂ to Rh. Subsequent reductive elimination of the secondary phosphine *via* P–P bond cleavage is proposed. Elimination of a second equivalent of phosphine regenerates the Rh(NacNac) fragment which then re-enters the catalytic cycle by reaction with P₂Ph₄.

In the case of the silylation reactions, an analogous catalytic cycle would generate equal amounts of Ph₂PH and Ph₂PSiR₃ for each P₂Ph₄ molecule activated. However, only low concentrations of Ph₂PH are observed by ³¹P{¹H} NMR spectroscopy of the catalytic silylation reaction mixtures. This suggests that the second part of the catalytic cycle, where Ph₂PH must dehydrocouple with a second equivalent of silane, is more rapid than the initial P₂Ph₄ activation. Reaction of P₂Ph₄ and two equivalents of Ph₂SiH₂ in the presence of 10 mol% of 1 at 50 °C for 5 days affords a 74% yield of the silylphosphine Ph₂P(SiPh₂H) and a 23% yield of Ph₂PH.

Independent experiments demonstrated such activation of P-H bonds. For example, exposure of Ph₂PH to 4 atm of D₂ in the presence of 5 mol% 1 led to hydrogen for deuterium exchange resulting in 85% conversion to Ph₂PD. While treatment of 1 with excess Ph₂PH generates a species in solution formulated as Rh(NacNac)(Ph2PH)2, dissociation of phosphine and oxidative addition of D₂, followed by reductive elimination of HD and Ph₂PD accounts for the observed deuteration. Similarly, heteronuclear dehydrocoupling of Ph2PH and silanes proceeds using 5 mol% of species 1. For example, reaction of Ph₂PH and Ph₂SiH₂ gave quantitative yield of Ph₂P(SiPh₂H) in 18 h at 50 °C. Similarly, Ph₂P(SiPhMe₂) is formed in 84% yield under similar conditions, while Ph₂P(SiPh₂Me) is formed in 85% yield in 18 h at 100 °C. As with the diphosphines, bulkier silanes afford lesser yields as Ph₂P(SiPh₃) is formed in only 40% yield from Ph₂PH and Ph₃SiH and the homo-dehydrocoupling by-product P₂Ph₄ is observed in 10% yield.

Overall, these data support a mechanism in which hydrosilylation of P_2Ph_4 affords both Ph_2PH and the silylphosphine; however the phosphine reacts further to form another equivalent of silylphosphine (Scheme 3). This latter P–Si dehydrocoupling is apparently faster than the initial P–P bond activation. Evidence for the nature of an intermediate was derived from stoichiometric reactions of 1 with Ph_2PH and Ph_2SiH_2 . In this case a short-lived species was observed spectroscopically. The ¹H NMR resonance at -13.5 ppm was indicative of a Rh–hydride species, while the doublet at 5.05 ppm indicated the presence of the PH bond of coordinated phosphine. These data together with the ³¹P{¹H} resonance at 47.4 ppm and the ²⁹Si{¹H} signal at 21.4 ppm were consistent with the formulation of **4** as



Scheme 3 Proposed mechanism of silvlation of P₂Ph₄ and PPh₂H.

(NacNac)RhH(SiHPh₂)(PHPh₂) (Scheme 2). This Rh(III) intermediate is analogous to the Ir complexes (NacNac)IrH₂(PR₃) isolated previously by Chirik and co-workers.³⁰ This intermediate is also related to CpRhH(SiR₃)(PR₃) complexes reported by Marder and co-workers.³¹ Loss of H₂ from this species would yield the proposed intermediate (NacNac)Rh(SiHPh₂)(PPh₂) which is proposed to undergo reductive elimination of the silyl–phosphide product. This proposition suggests that reductive Si–P elimination occurs more readily than ligand redistribution reactions.

In summary, the Rh-catalyst derived from **1** effects the catalytic hydrogenation and silylation of diphosphines. Inherent in this chemistry is the dehydrocoupling of secondary phosphines with silanes. Further studies of the mechanism, catalyst optimization and applications of these processes are ongoing.

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Notes and references

‡ Preparation of 2 and 3: these compounds were prepared in a similar fashion and thus only one preparation is detailed. To a solution of 30 mg (0.081 mmol) P₂Ph₄ in 5 mL of toluene was added a solution of 50 mg 1 (0.079 mmol) in 5 mL of toluene. The mixture was allowed to stir overnight upon which the solvent was removed in vacuo. The dark-red residue was washed with 10 mL cold pentane to give 35 mg of the product 2 (0.039 mmol, 50% yield). ¹H NMR (C₆D₆) δ : 0.84 (6H, d, J = 6.5 Hz), 1.20 (6H, d, J = 6.5 Hz), 1.71 (6H, s), 4.45 (4H, sept, J = 6.5 Hz), 5.15 (1H, s), 6.73–7.19 (26H, br m). ³¹P{¹H} NMR (C₆D₆) δ : –51.4 (d, J_{P-Rh} = 140 Hz). ¹³C NMR (C_6D_6) δ : 24.0, 24.4, 28.6, 98.0, 124.0, 124.1, 127.5–128.6 (m, obscured by C_6D_6), 128.9, 134.9 (app. t, J = 7.5 Hz), 157.7, 159.6. EA anal. calcd for RhP₂N₂C₅₃H₆₁ (%) C: 71.21, H: 7.22, N: 3.13; found: C: 70.91, H: 7.22, N: 2.72. X-Ray quality crystals were grown by slow evaporation from a pentane solution. M = 890.89, space group: monoclinic, $P2_1/n$, a =10.8591(11), b = 35.296(4), c = 12.6312(13) Å, β = 94.769(2)°, V = 4824.6(9) Å³, Z = 4, T = 273(2) K, data: variables 8472: 525, R = 0.0484, $R_{\rm w} = 0.1099$, GOF = 1.053; CCDC 658230. 3: ¹H NMR (C₆D₆) δ : 0.74 (8H, app. pent, J = 7.8 Hz), 1.26 (12H, t of d, J = 7.3 Hz, 2.9 Hz), 1.35 (12H, d, J = 6.9 Hz), 1.63 (12H, d, J = 6.9 Hz), 1.84 (6H, s), 4.19 (4H, sept), 4.19 (4H, sept), 1.84 (6H, s), 1.84 (6H, sJ = 6.9 Hz), 5.19 (1H, s), 7.15–7.29 (6H, m). ³¹P NMR (C₆D₆) δ : -64.51 (d, J = 127 Hz). ¹³C NMR (C₆D₆) δ : 9.8, 12.9, 22.4, 23.9 (d, J = 9.6 Hz), 28.3, 97.0, 123.2, 123.8, 127.3-130.5 (m, obscured by C₆D₆), 140.3, 156.7, 159.4. EA anal. calcd for RhP₂N₂C₃₇H₅₅ (%) C: 63.32, H: 9.19, N: 3.99; found: C: 63.55, H: 9.24, N: 4.12. X-Ray quality crystals were grown from a pentane

solution at -30 °C. M = 698.73, space group: monoclinic, $P\overline{1}$, a = 10.566(3), b = 11.676(4), c = 17.636(6) Å, $\alpha = 102.412(4)$, $\beta = 93.045(4)$, $\gamma = 114.125(4)^\circ$, V = 1914.7(11) Å³, Z = 2, T = 296(2) K, data: variables 6726: 381, R = 0.0459, $R_w = 0.1233$, GOF = 0.969; CCDC 658231. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712972f

Generation of 4: to 20 mg 1 (0.032 mmol) in 2 mL toluene was added 12 mg Ph₂SiH₂ (0.064 mmol). The solution was cooled to -30 °C upon which 6 mg Ph₂PH (0.032 mmol) was added. The solution was allowed to warm to room temperature, volatiles were removed *in vacuo* and the residue was washed with pentane (2 × 2 mL), leaving 12 mg of 4 (0.013 mmol, 43% yield). ¹H NMR (C₆D₆) δ : -13.5 (1H, d of d, J_{H-P} = 28.4 Hz, J_{H-Rh} = 15.4 Hz), 0.23 (3H, d, J = 6.6 Hz), 0.62 (3H, d, J = 6.6 Hz), 1.11 (3H, d, J = 6.6 Hz), 1.04 (3H, d, J = 6.6 Hz), 1.06 (3H, d, J = 6.6 Hz), 1.15 (3H, s), 1.88 (3H, s), 2.76 (1H, sept, J = 6.6 Hz), 2.82 (1H, sept, J = 6.6 Hz), 4.07–4.16 (2H, ov sept, J = 6.6 Hz), 5.00 (1H, d, J_{H-Rh} = 36 Hz), 5.05 (1H, d, J_{P-H} = 361 Hz), 5.34 (1H, s), 6.35–7.61 (26H, ov m). ³¹P{¹H} NMR (C₆D₆) δ : 21.4 (d of d, J = 23.5 Hz, J = 34.1 Hz).

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